

Development of New Electrolytes for Lithium-Sulfur Batteries



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Overview

Timeline

Project started: FY 2020
Project end date: FY 2022
Percent complete: 20%

Budget

Total project funding
-DOE share: \$1,884K, 100%
FY20 funding \$628K
FY21 planned funding \$450K

Barriers Addressed

Performance: Low energy density and poor cycle life
Life: Poor calendar life

High materials and cell cost

Partners

LBNL (Dr. Chenhui Zhu, Dr. Jinghua Guo, Dr. Wanli Yang, and Dr. Ling-Wang Wang)
UC Berkeley (Prof. Andrew Minor)
General Motors (Dr. Mei Cai)
Texas A&M University (Prof. Perla Balbuena)

Relevance – Project objective

This proposed work aims to develop new electrolyte and additives to enable sulfur material as a high capacity and long cycle-life material for positive electrode and lithium metal as negative electrode, to address three of the barriers of energy storage device for EV/PHEV application, insufficient energy density, poor cycle life performance, and poor calendar life.

1. Develop new electrolytes and additives to for Li-S battery
2. Understand the fundamental properties of the electrolytes and additives.
3. Develop electrode assembly strategies to overcome the electrode level failures.
4. Demonstrate the performance improvement via electrode and cell level testing and analysis.

Relevance – Project objective

This work addresses the adverse effects of polysulfide dissolution, lithium dendrite formation and minimizes the side reactions to significantly improve capacity and lifetime of Li-S battery. The research and development activities will provide an effective electrolyte formulation to prevent polysulfide dissolution and suppress lithium dendrite formation. This work will also provide an in-depth understanding of the properties of the new electrolyte and additives.

Project Objective

Develop new electrolytes, additives and electrode compositions for Li-S battery with high ion-conductivity, stable towards polysulfide, and promoting the polysulfide affiliation with the electrode substrate to prevent polysulfide dissolution, and promoting dendrite-free lithium metal deposition.

Project Impact

To address the high cost and low energy-density of the Li-ion rechargeable batteries. The emerging Li-S batteries could be both high energy-density and low cost. This project enables the applications of low cost and abundant sulfur element as a major chemical component for electrical energy storage. This project will develop new approaches for electrolytes and electrode compositions of Li-S rechargeable batteries.

Milestones

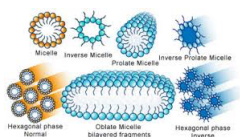
FY 2020

1. Use the synchrotron analyses in studying the new electrolytes. (Timeline: Q1, complete)



Use synchrotron based X-ray diffractions

2. Characterize and optimize the new electrolytes. (Timeline: Q2. complete)



Understand micelle formation and structures

3. Study the cycling properties of sulfur electrode and lithium metal electrode under the new electrolytes. (Timeline: Q3, in progress)

Characterize the electrochemical performance and electrode morphologies

4. Select two electrolyte compositions to test in Li-S battery. (Timeline: Q4, in progress)

Further testing of the electrolytes

Note: This project is FY2020 new start

Approaches

Use material design and synthesis to develop new electrolytes and additives for Li-S rechargeable battery. Use advanced diagnostics such as synchrotron based X-ray diffractions and battery testing to characterize the new electrolytes.

1. Develop new electrolytes and additives for Li-S battery. The properties of the ideal electrolyte for sulfur electrode would be high ion conductivity, stable towards polysulfide, and promoting the polysulfide affiliation with the electrode substrate to prevent polysulfide dissolution.
2. Chemically modify the structures of the additives, electrolyte solvents and salts to increase electrolyte stability and ionic conductivity and to prevent polysulfide dissolution and promote polysulfides precipitation.
3. Use synchrotron based X-ray diffractions to characterize the micro and nanostructure of the electrolyte, and use electron microscopy to characterize the morphology of the electrode.
4. Use classic electrochemical testing methods to characterize the Li-S battery performance based on this new class of electrolyte.

This work will be a collaboration with the LBNL synchrotron facility - the Advanced Light Sources to continue our effort to develop Li-S in situ electrochemical cell for the analysis of polysulfide dissolution and precipitations during electrochemical process. The new electrolyte structure/composition will be integrated and analyzed in the synchrotron based in situ cell.

ALS - LBNL



Accomplishments – New electrolytes and additives design strategy for Li-S battery

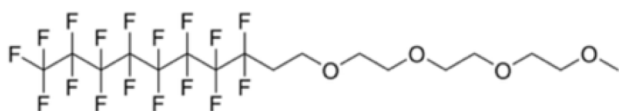
Strategy: amphiphilic fluorinated additives in hydrofluoroether (HFE) solvents

Amphiphilic fluorinated additives: bi-functional structure of lithiophilic head (EO) and lithiophobic tail (fluorocarbon).

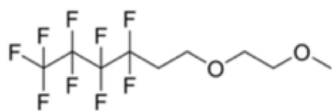
Solvation mechanism: micelle formation

Polysulfide suppression in HFE solvents

Li metal stabilization in HFE solvents



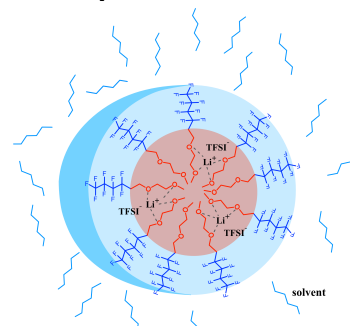
Synthetic Molecule 1



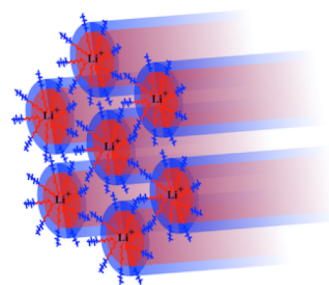
Synthetic Molecule 2

F_8EO_4 (molecule 1) & F_4EO_2 (molecule 2)

Possible micelle structures
Spherical

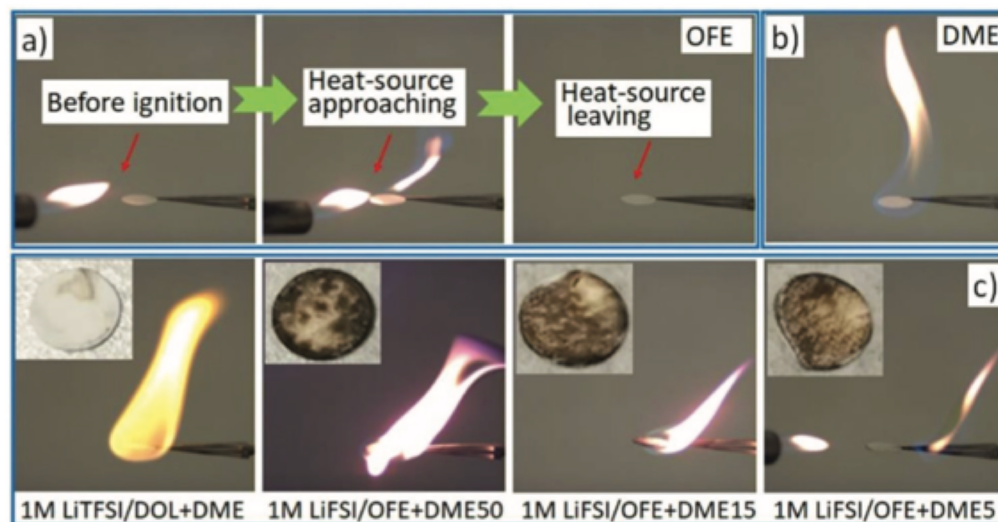
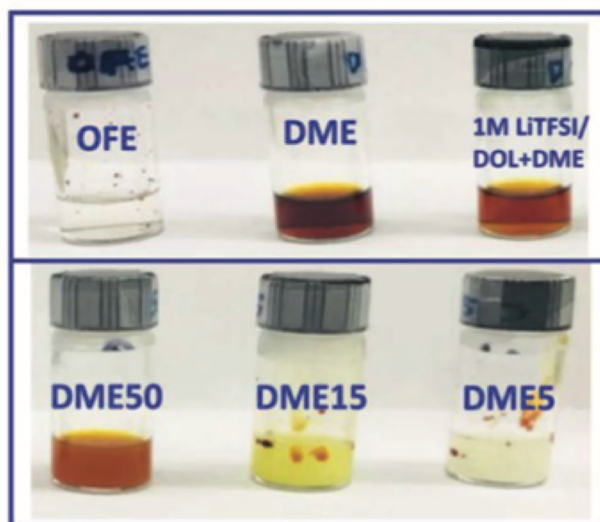


Hexagonal



Accomplishments – The advantages of hydrofluoroether (HFE) solvents

Less polysulfide dissolution and low flammability



suppressed polysulfide dissolution

flammability of ether based electrolytes

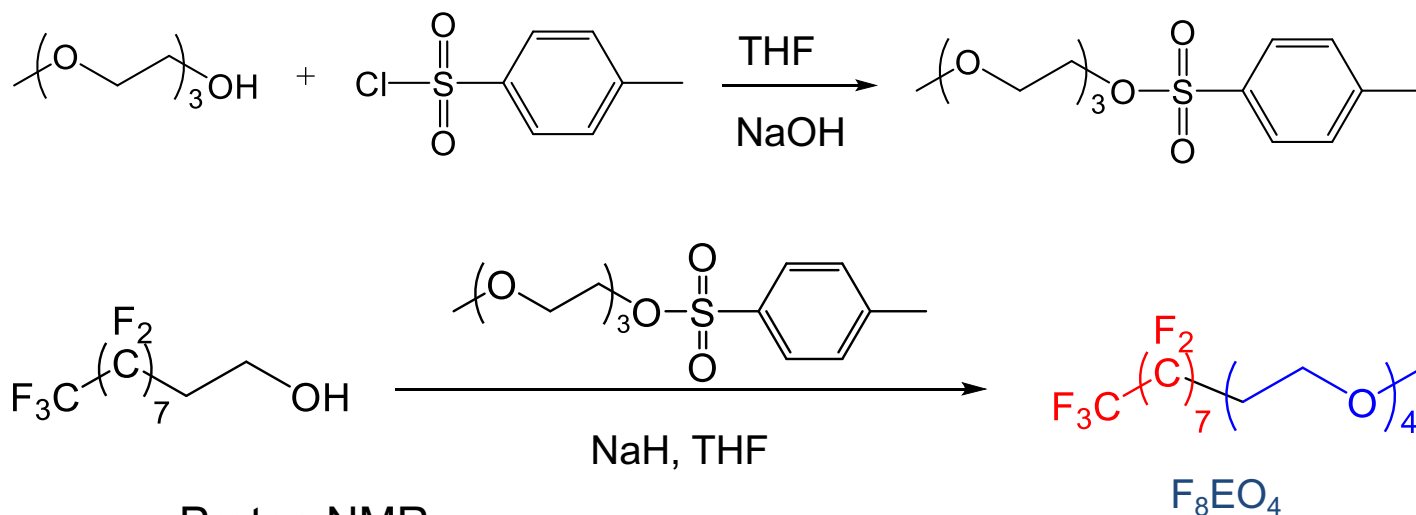
	Non-fluorinated					TTE	
	<chem>CCOCC</chem>	<chem>CC(F)(F)OCC(F)(F)F</chem>	<chem>CC(F)OCC(F)F</chem>	<chem>CC(F)OCC(F)F</chem>	<chem>CC(F)OCC(F)F</chem>	<chem>CC(F)OCC(F)F</chem>	<chem>CC(F)OCC(F)F</chem>
LiTFSI:	0	5.5	5.6	6.9	7.6	15.6	
Li ₂ S ₆ :	0	4.3	5.2	6.3	8.4	13.8	

Relative binding energy of LiTFSI and Li₂S₆

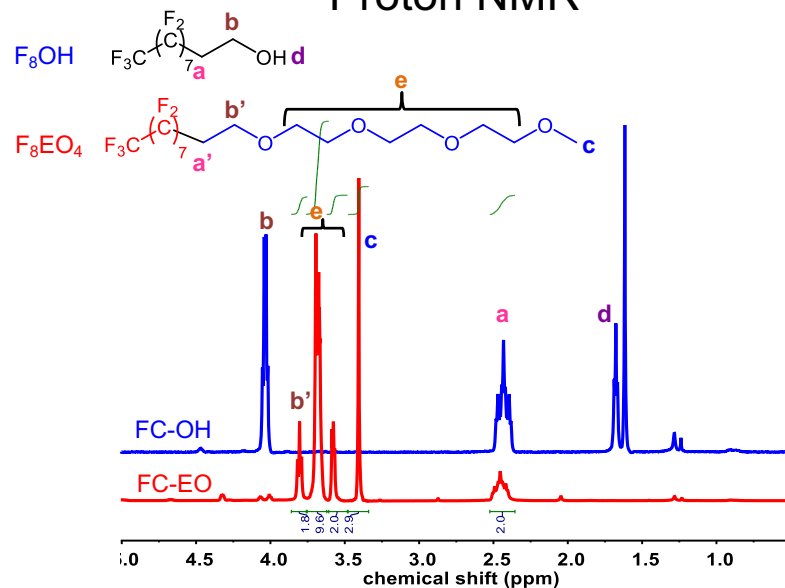
Ref: Zheng et al. Adv. Energy Mater. 2019, 9, 1803774

Accomplishments – Synthesis of the amphiphilic additives

Synthesis scheme



Proton NMR



Both F_8EO_4 (molecule 1) & F_4EO_2 (molecule 2) are successfully synthesized based on established procedure with slight modification.

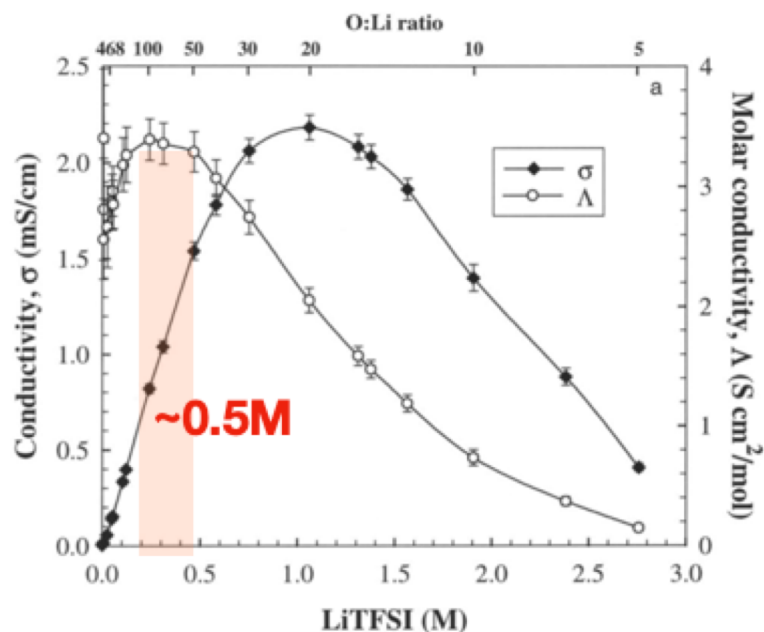
Example shown here is F_8EO_4 (molecule 1)

Ref: J. Org. Chem. 2018, 83, 1903–1912

Accomplishments – New electrolyte formulations, conductivity and viscosity

Ionic conductivity of 0.5M LiTFSI electrolytes based on various amphiphilic additives and TTE ratios

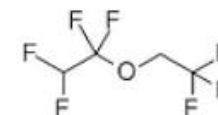
Amphiphilic additives : TTE* by volume	σ (mS/cm)	
	F ₄ EO ₂	F ₈ EO ₄
1:1	3.2	0.61
1:5	1.05	0.35



Finally, select 0.5M LiTFSI electrolytes

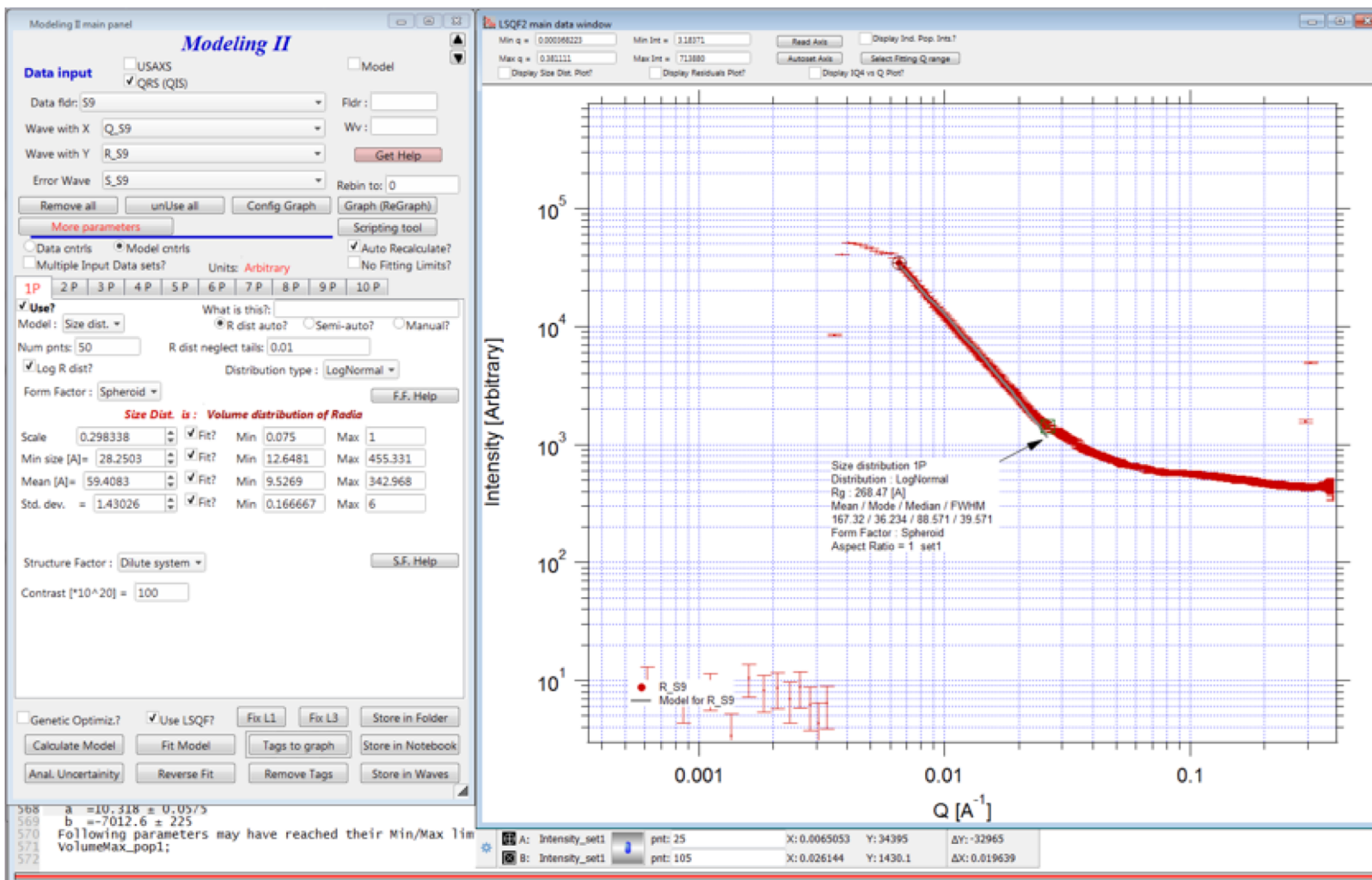
- 4.0M sat. solubility but too viscous for battery fabrication
- 0.5M with highest conductivity (literature)
- diluted with TTE
- small molecule with larger conductivity

*TTE: 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether



Ref: Walls et al. J Electrochem. Soc. 2003, 150, E165-174

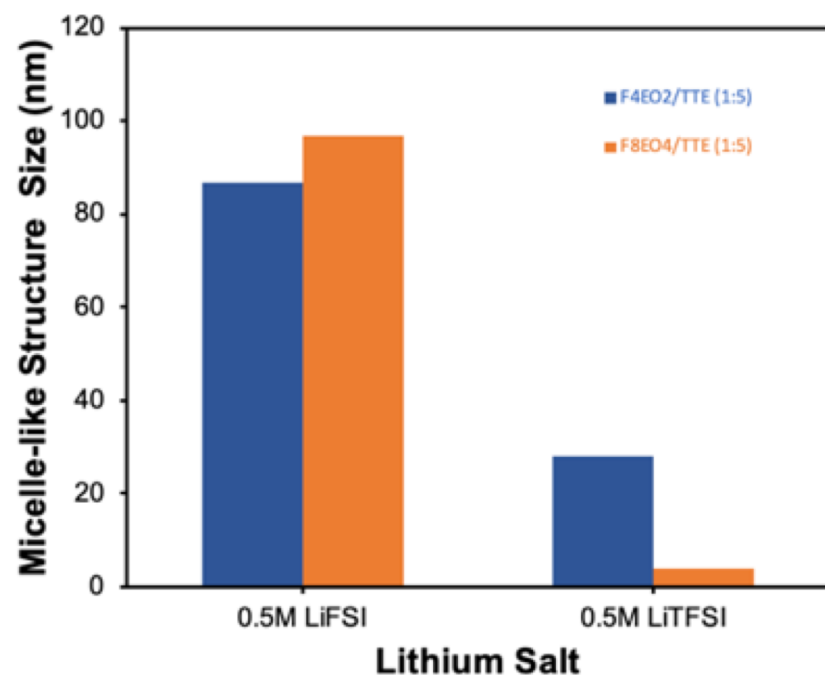
Accomplishments – Using synchrotron based small angle X-ray scattering (SAXS) to characterize the electrolyte micelle structures



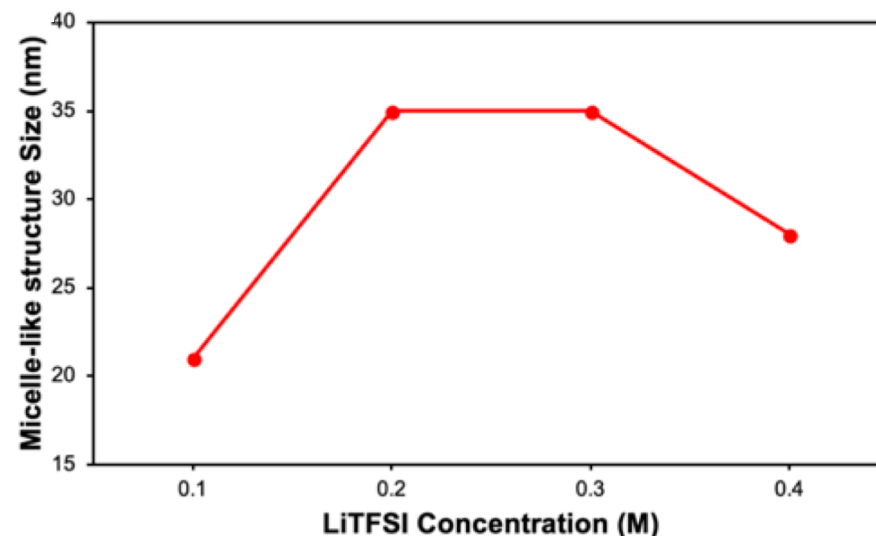
Micelle size distribution analysis at the synchrotron facility ALS - LBNL

Accomplishments – Micelle size based on type of additives and lithium salts

Micelle size matrix



Micelle size distribution vs. lithium salt concentration

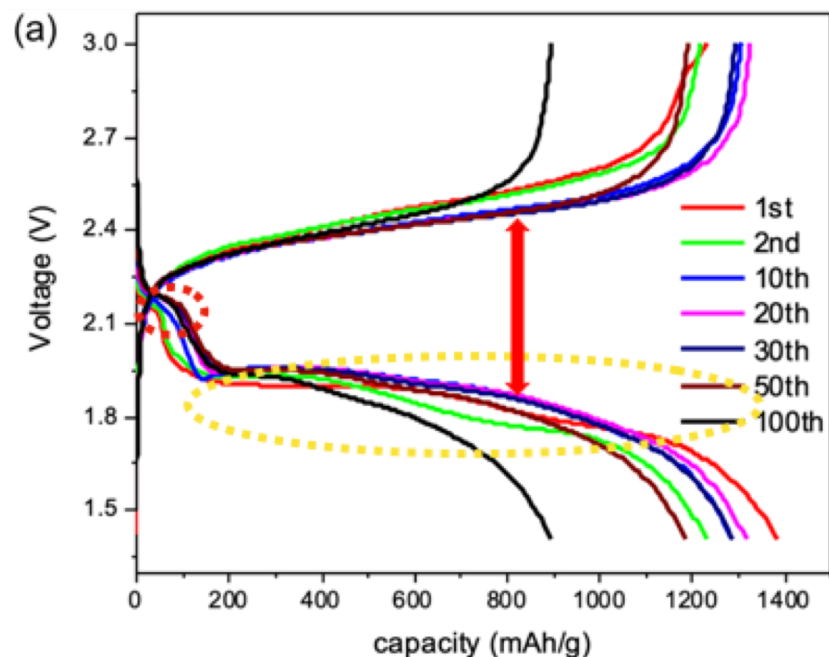


- Lithium salts play a significant role in micelle structure
- Micelle size tends to be bigger for LiFSI than that of LiTFSI
- Micelle size changes with salt concentration

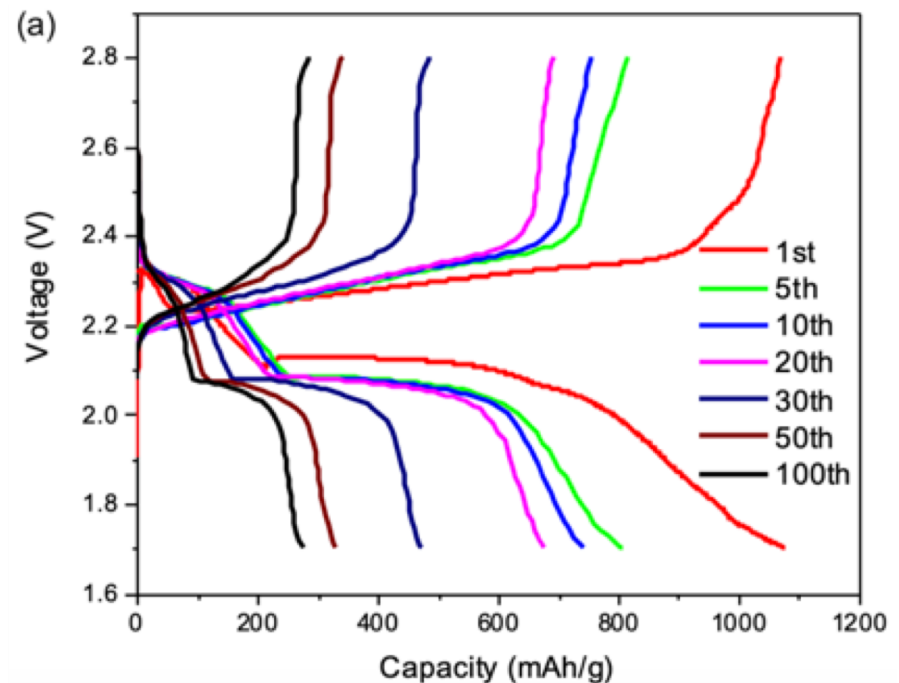
Accomplishments – The electrochemical performance of the new electrolytes

Voltage Profile: F_4EO_2/TTF vs. DOL/DOE

0.5M LiTFSI in $F_4EO_2:TTE(1:5)$



1.0M LiTFSI in DOL/DME



Pros-Polysulfide suppression evidenced by:

- Small percentage of 1st discharge plateau (occurs below 2.3V)
- large initial capacity
- better cycling stability

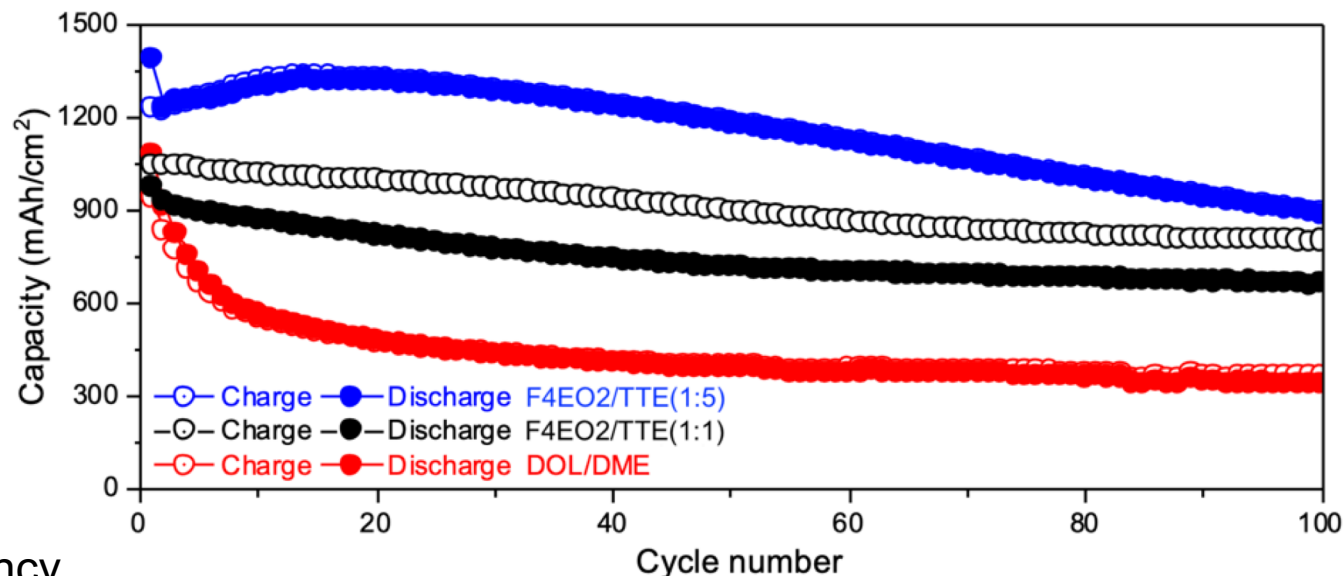
Cons-the larger polarization suggests sluggish kinetics

Accomplishments – The electrochemical performance of the new electrolytes

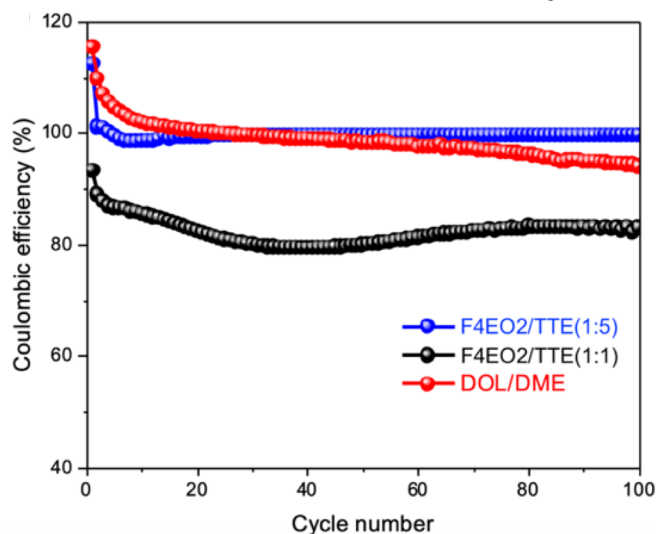
Li-S battery

The sulfur electrode performance

Cycling performance



Coulombic efficiency

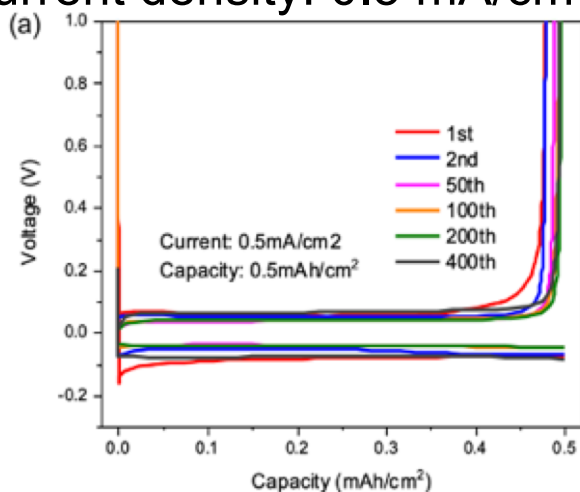


F₄EO₂/TTE(1:5) electrolyte shows the optimum performance

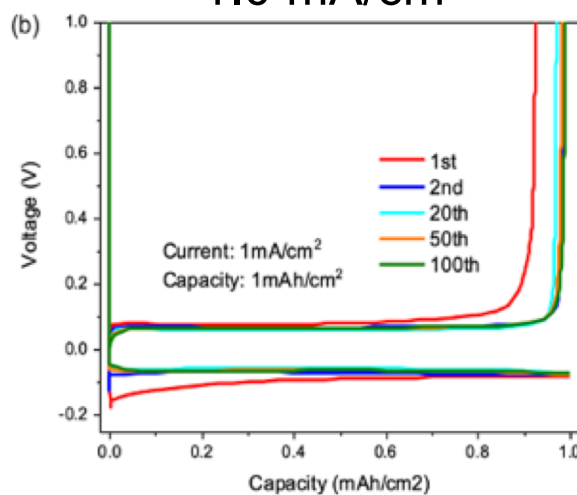
- 1395 mAh/g initial discharge capacity
- 71.9% over 100 cycles
- >99.5% CE over 100 cycles

Accomplishments – Lithium plating and stripping properties based on the new electrolytes: F_4EO_2/TTE (1:5), 0.5M LiFSI

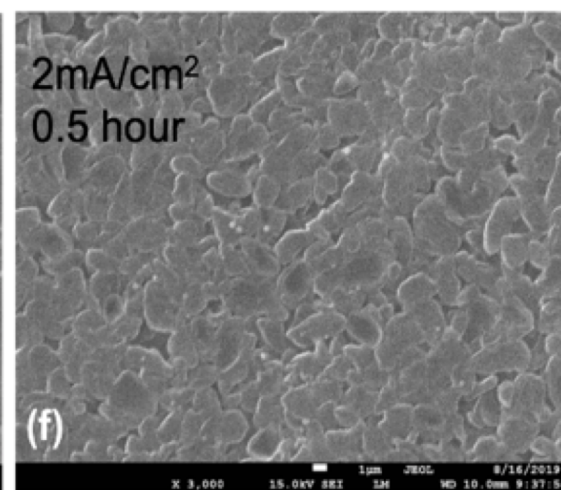
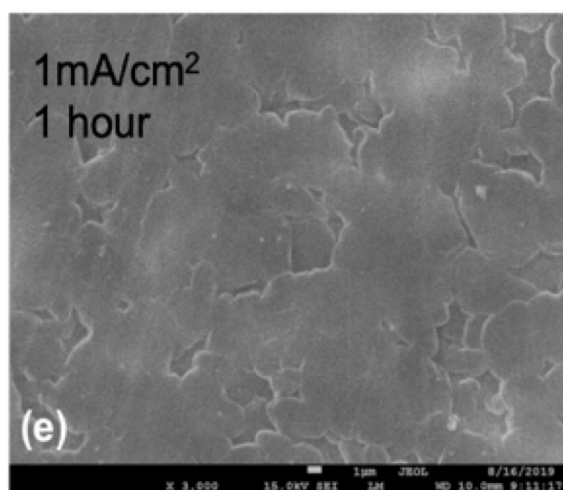
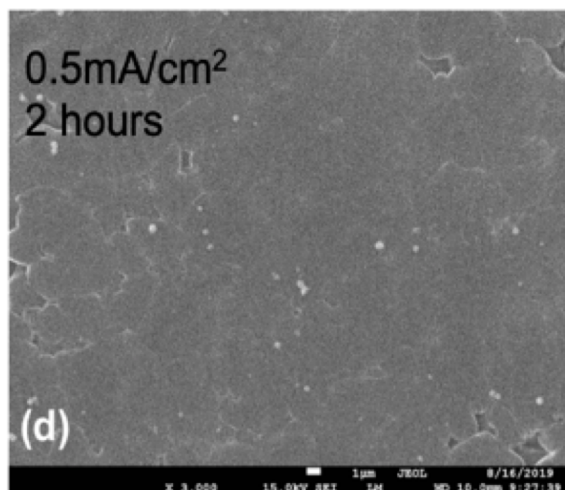
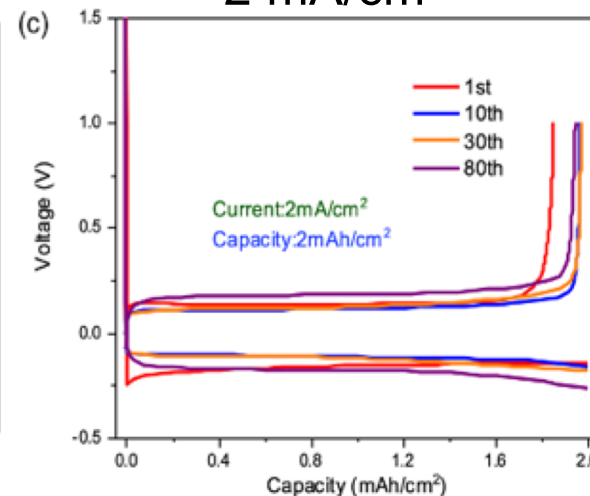
Current density: 0.5 mA/cm²



1.0 mA/cm²



2 mA/cm²



No dendrite



Large granular structures

Responses to Previous Year Reviewers' Comments

This project was a new start in FY 2020, and not reviewed last year.

Collaborations and Coordination With Other Institutions

1. Lawrence Berkeley National Laboratory

In collaboration with synchrotron physicist Dr. Chenhui Zhu, Dr. Jinghua Guo and Dr. Wanli Yang to develop in situ cell in the beamline for the X-ray characterization to quantify the electrolyte micelle structures, polysulfide dissolution and precipitation.

In collaboration with BMR PI Dr. Ling-Wang Wang to conduct simulation on the polysulfide dissolution in the new electrolyte system.

2. UC Berkeley

In collaboration Prof. Andrew Minor to characterize the sulfur electrode 3D structure before and after cycling. We will use FIB and lift-out technology to prepare the cross-section of the composite electrode, and use TEM and SEM to analysis the micro and nano-structures.

3. Texas A&M University

Prof. Perla Balbuena's group will conducting simulation on the polysulfide interaction with the electrode matrix in the new electrolyte. One of her students is taking a 3-month-stint in my group at Berkeley Lab to learn experimental details of Li-S battery. Prof. Balbuena is a BMR PI.

4. General Motors

General Motors will provide electrolyte and cell testing to verify the Li-S performance. GM is a partner of the VTO funded institution.

Remaining Challenges and Barriers

1. Although the team is scheduled to accomplish all the FY2020 milestones at the end of this year, the Lab shutdown due to the COVID-19 posts a challenge to accomplish all the milestones on time.
2. The team worked at ALS to conduct X-ray diffraction measurement in the first quarter based on a rapid access proposal to the LBNL synchrotron facility. A full proposal is currently in the review process. The team will have more beamline time to use the facility once the proposal is accepted and activated. A more detailed and systematic structure study of the new electrolyte is planned.
3. Although high sulfur utilization at 1200 mAh/g-S is achieved, more rigorous testing and control experiments are planned to fully characterize the new electrolyte and electrochemical performance.
4. Understand the lithium internal microstructure after lithium deposition will need to use cryo-TEM technique. The team is currently working with The Molecular Foundry to explore the cryo-TEM capabilities.

Proposed Future Work

Future milestones for this project for FY2020 and FY2021.

FY 2019

1. Use the synchrotron analyses in studying the new electrolytes.
2. Characterize and optimize the new electrolytes.
3. Study the cycling properties of sulfur electrode and lithium metal electrode under the new electrolytes.
4. Select two electrolyte compositions to test in Li-S battery. Go/No-Go: sulfur utilization > 1200 mAh/g

FY 2020

1. Generate a library of the composition of the new electrolyte, measure their structure properties using X-ray diffraction method.
2. Measure the conductivities and transport properties of the new electrolytes.
3. Measure the microstructures of the lithium metal and sulfur electrode in a cycled Li-S battery using the new electrolyte.
4. Pilot scale up synthesis of one composition of the new electrolyte and delivery to other national lab for testing. Go/No-Go: sulfur utilization > 1400 mAh/g.

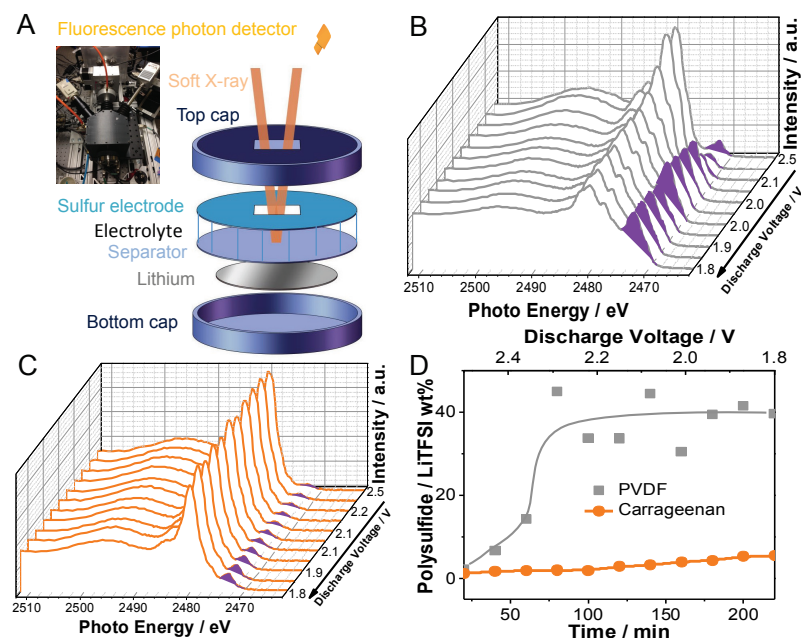
Any proposed future work is subject to change based on funding levels.

Summary

- Developed amphiphilic additives, hydrofluoroether solvents, and lithium salts based new electrolytes for Li-S battery.
- Characterized the unique micelle solvation mechanism of the electrolyte via SAXS method.
- Identified F_4EO_2 :TTE at 1:5 ratio electrolyte exhibits superior cycling stability and high Coulombic efficiency
- Future work is planned for further characterization of the new electrolytes as well as the S and Li electrodes after cycling.

Technical Back-Up Slides

Previous results on operando XAS measurements of Li-S cell

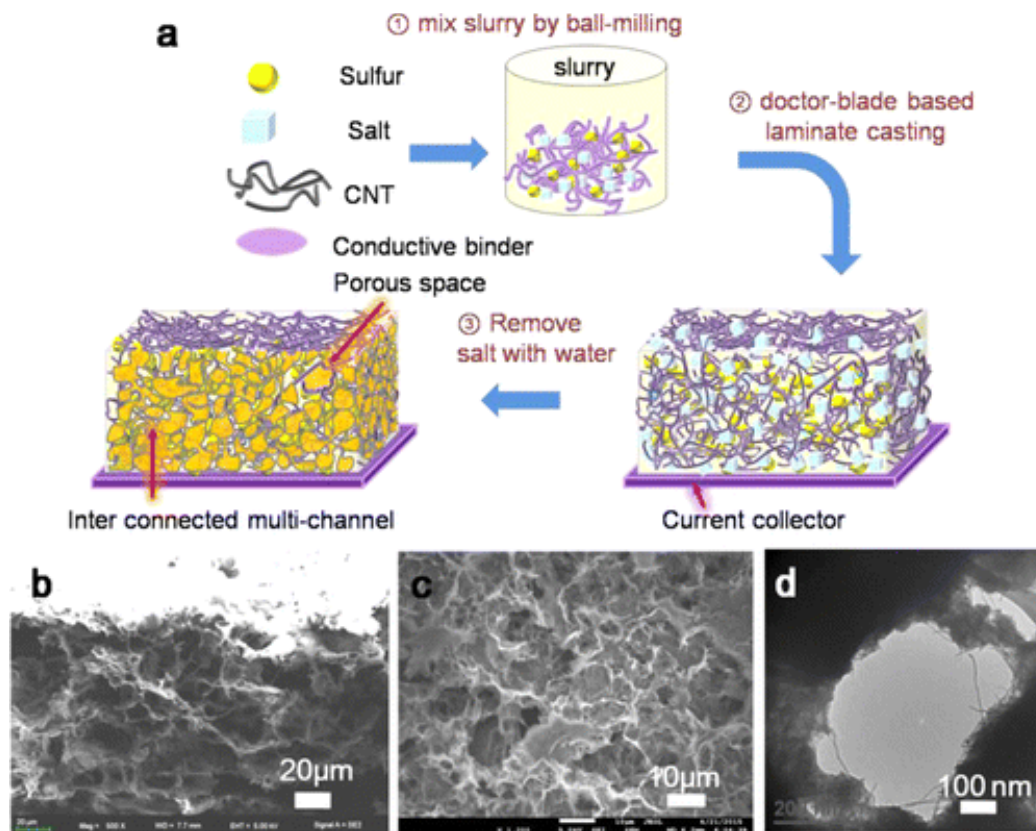


Operando XAS measurements of Li-S cell. (A) Schematic of the *in situ* XAS measurement set-up. The inset photo is the actual customer build instrumentation for this experiment. (B,C) The S K-edge XAS spectra evolution of the electrolyte with voltage scan. The purple highlighted peaks are polysulfide adsorption peaks, which evolve during first discharge. PVDF binder based Li-S cell shows the dramatic increase of polysulfide concentration in the electrolyte during the first lithiation process. The carrageenan binder based Li-S cell shows much slow concentration built up of polysulfide. D) The relative polysulfide concentration changes with discharge shows the superiority of carrageenan binder in immobilizing polysulfide.

Liu et al. Nano Energy 38 (2017) 82-90

Technical Back-Up Slides

Previous approach on sulfur electrode design



(a) Schematic illustration of the porous ant-nest structure Li-S electrode (CNT-nest-S) fabrication procedure. SEM cross-section (b) and top (c) morphology of CNT-nest-S. (d) The TEM morphology of the pore in the fully discharged CNT-nest-S.